Electrochemical Oxidation of Dissolved Carbon Monoxide on Gold Electrode in Alkaline Medium

Andrew S. Lin*, Johnny Lin*, and Jerry C. Huang+

* Dept. of Chemical and Materials Engineering, Chang Gung University
259 Wen-Hwa 1st Rd., Kwei-Shan, Tao-Yuan, TAIWAN 333
+ Institute of Materials Science and Nanotechnology, Chinese Cultural University, Taipei, TAIWAN 111
*Corresponding author: Andrew@mail.cgu.edu.tw
+ h646919@ms47.hinet.net

Abstract

The study of the oxidation of dissolved CO is not much seen in the literature probably due to the strong adsorption of CO on platinum metals in acidic media. This work was thus undertaken to study the electrochemical oxidation of dissolved CO on Au in alkaline medium without the influence of adsorbed CO. Our results show that the electrochemical oxidation of dissolved CO on gold electrode is mainly diffusion-controlled process at the potential greater than 0.3V (vs. RHE). At the potential range between 0.0V and 0.3V, the oxidation process is a mixed-control process. Our data also confirm that the electrochemical oxidation of dissolved CO is affected by the presence of surface oxide on gold. The electrochemical oxidation of the dissolved CO at liquid-solid interface may provide certain practical uses in CO removal or low temperature fuel cell.

Alkaline Fuel Cell (AFC) was potentially considered as a power source in the past. The disadvantage of this system is that it limits itself to fuels and oxidants without carbon dioxide. The technology of alkaline fuel cell system can be greatly improved from the progress made in PEFC technology especially in materials. The advantages of alkaline fuel cell are: (1) much less polarization in the air electrode, (2) using low-cost non-noble metal catalysts such as Ag, Ni, Au or CoTMPP, (3) less crossover problem due to the electro-osmosis of hydroxide ion rather than hydrogen ion, (4) less carbon dioxide problem when employing alkaline anion-conducting polymer electrolyte.

The electrocatalysis of methanol and carbon monoxide oxidation in acidic media has been studied and modifications of platinum with some metals like ruthenium are proposed in previous works[1-4]. The reaction of surface adsorbed CO and CO-like species from stepwise dehydrogenation of methanol with the surface oxide of platinum is believed to be the surface reaction of the electrochemical oxidation of carbon monoxide. The dissolved carbon monoxide in the bulk of solution exhibits some effects on the oxidation of adsorbed CO [5] but the study of the oxidation of dissolved CO is not much seen in the literature probably due to the strong adsorption of CO on platinum metals. The adsorption of CO on gold may be weaker than that on platinum. This work was thus undertaken to study the electrochemical oxidation of dissolved CO on Au with the minimal influence of adsorbed CO if possible.

Although the electrochemical oxidation of carbon monoxide on gold electrodes had been studied since 1960[6,7], most of papers discuss the surface adsorbed CO and the effects of gold surface conditions on the oxidation potentials of adsorbed CO [8, 9, 10]. The electrochemical oxidation potential of surface adsorbed CO on gold are much more positive (0.3V to 0.5V vs. RHE) than solution phase CO (0.1V vs. RHE in this paper) depending on experimental conditions[11] and there is no clear report discussing the electrochemical oxidation of the mass transfer phenomena of solution phase CO to gold electrode.

Experimental

The oxidation potentials of CO adlayers on platinum in the stripping voltammetry are a function of the holding potential[5], suggesting that the conditions for CO adsorption on metal surface are critical. Similarly, cyclic voltammetry of electrochemical oxidation of CO on gold in alkaline media also exhibits oxidation currents that depend on the surface adsorbed CO and dissolved CO at a certain potential range. In this study, a rotating gold electrode was used to study the electrochemical oxidation of dissolved CO. The experimental conditions are discussed in the following.

The solution of 1 M potassium hydroxide (KOH) by using deionized water and KOH from Showa chemicals or Riedel-deHaen was deoxygenated by rapidly bubbling nitrogen or carbon monoxide through the electrolyte for more than

60 minutes and this electrolyte was then used for experiments while nitrogen or carbon monoxide was purged above the liquid level to keep the air away. A mercury/mercury oxide reference electrode was used in this alkaline system and all figures used in this paper were adjusted to the RHE by using 0.926V vs. NHE scale and carefully calibrated with saturated calomel electrode in 0.685V vs NHE scale occasionally. The oxide formation potential in voltammetry of gold can also be judged the corrected potential scale. A Pine rotating gold disk electrode with a geometric area of 0.19625 cm^2 was used for the experiments. This gold disk electrode was cycling in the CV potential window (0.05V to 1.4V vs. RHE) more than 20 times for obtaining a typical voltammetry of gold before preceding the experiments. The effects of potential windows (potentials cycling up to 0.8V and 1.1V vs. RHE) in voltammography were also observed in the Figure 4 and discussed later. The Pine Instrument rotating electrode controller and Princeton Applied Research/AMETEK PARSTAT® 2263 potentiostat were used for the voltammetry measurements.

The rotating disk electrode experiments were carried out in 1 M KOH that was saturated with 10^{-3} M CO gas, and the negligible carbonation effect was observed when 10^{-4} M CO_2 gas was intentionally added into the electrolyte during cyclic voltammetry. The procedure employed was: cyclic voltammograms were recorded at a sweep rate of 20 mv/sec while the rotating speed was maintained at 400, 900, 1600 and 2500 rpm. In order not to record the voltammograms of electrochemical oxidation of surface adsorbed CO, the first potential scan of the first rotating speed was not used. The potentials were kept cycling while each rotating speed was changed and the voltammograms were recorded either from a lower rotating speed to a higher speed or vice versa. When the steady state of forced convection was reached, then the voltammograms were recorded in forward and backward directions.

Results and Discussion

The hydrogen adsorption and desorption, regularly seen on platinum, is not observed on gold metal. So the co-adsorption of surface adsorbed CO and adsorbed H atom was not observed in our system. The use of oxide-free potential range in cyclic voltammetry to record the oxidation current of dissolved CO is the main feature of our study.

The oxidation currents of dissolved CO (10^{-3} M) on gold electrode in 1 M KOH exhibit pure diffusion control behavior as shown in Figure 1. The limiting currents of each rotating speed are reproducible and the currents follow the Levich equation (see the insert). The plot of limiting electrochemical current at given angular rotating speed was taken in the variation of the limiting current with potentials (0.5V, 0.6V, 0.7V, 0.8V and 0.9V vs. RHE) at different values of angular rotating speeds (400 rpm to 2500 rpm) and a linear plots are obtained as the limiting current against root square of angular rotating speed (20, 30, 40 and 50). The intercept

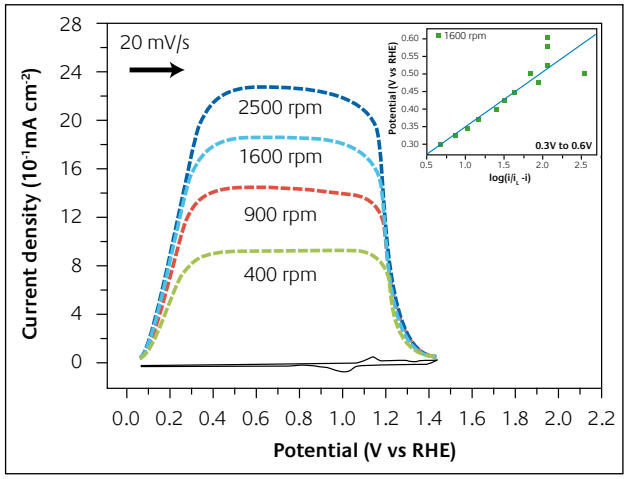

Figure 1

Rotating Disk data of gold disk in 1 M KOH saturated with 10^{-3} M CO (solid line/no rotating) at rotating speeds of 400, 900, 1600 and 2500 rpm. (Positive potential scan recorded). The insert of limiting current corrected plot indicates the diffusion-controlled behavior of the oxidation currents at the potentials greater than 0.3V (vs. RHE).

Table 1

The numbers taken from a plot of inverse currents against root square of angular rotating speed in the rotating gold disk in 1 M KOH saturated with 10^{-3} M CO at rotating speeds of 400, 900, 1600 and 2500 rpm.

	I ($1*10^{-4}$ A/cm^2) current density				
Potentials	0.5 V	0.6 V	0.7 V	0.8 V	0.9 V
400 rpm	9.17	9.22	9.27	9.27	9.22
900 rpm	14.57	14.62	14.73	14.57	14.27
1600 rpm	18.45	18.70	18.65	18.55	18.34
2500 rpm	22.57	22.73	22.73	22.52	22.32
Slope	2.16	2.15	2.13	2.12	2.13
n (charge transfer numbers)	2.14	2.14	2.12	2.10	2.11

of this linear plot is close to zero with little kinetic current contribution and the slope of this linear plot contribute to mass transfer limiting current of at plot-taken potential range (0.5V to 0.9V). A linear plot of inverse current vs. inverse of root square of angular rotating speed can be used to determine the approximate numbers of electron transfer in the electrochemical oxidation of solution phase CO on gold electrode (Table 1). The number of electron transferred in the reaction is calculated to be close to 2 using Levich equation and 10^{-3} M as the concentration of dissolved CO. Similar situation was found when the dissolved CO concentration was changed to 10^{-4} M. Figure 2 shows the oxidation currents of 10^{-3} M, 5 x 10^{-4} M and 10^{-4} M CO in 1 M KOH using a rotating speed of 1600 rpm, and the currents are proportional to the concentrations of dissolved CO in the electrolyte.

When the cyclic voltammograms were recorded without rotation, the oxidation currents of dissolved CO (10^{-3} M) on gold electrode in the first potential scan have oxidation

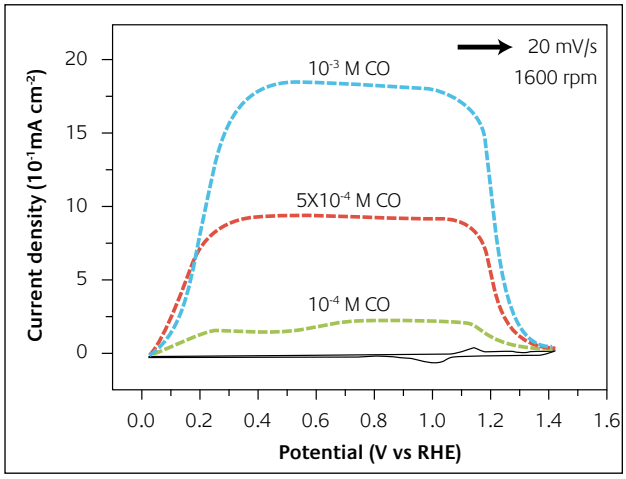

Figure 2

Rotating Disk data of gold disk at 1600 rpm in 1 M KOH with 10^{-3} M, 5 x 10^{-4} M and 10^{-4} M CO. (Positive potential scan recorded; solid line/no rotation).

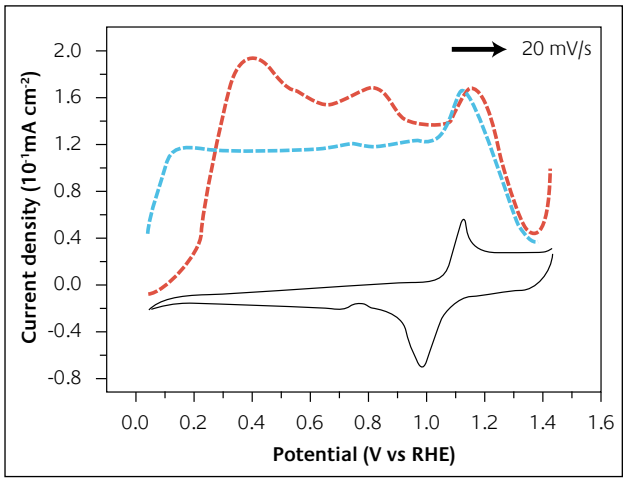

Figure 3

Voltammogram of gold disk in 10^{-3} M CO saturated 1 M KOH without rotation. Red line: first potential scan and blue line: the 2nd and the following potential scans (all are superimposed). (Positive sweep recorded; solid line/CO free).

peaks different from those in the 2nd scan and the scans followed [see Fig.3]. The first potential scan indicates that the electrochemical oxidation of the dissolved CO is retarded by the presence of adsorbed CO on gold surface and the retarded oxidation potential starts around 0.3 V (vs. RHE), 0.2 V more positive than that in the absence of adsorbed CO. The electrochemical oxidation of adsorbed CO requires an oxygen-containing species to form CO2, either from gold surface oxide or from any oxygen-containing species near the gold surface. The adsorbed CO shows more positive oxidation potential than that of dissolved CO, indicating the difficulty in oxidizing adsorbed CO.

An investigation was performed by excursing the electrode potentials before and after the oxide formation to see the effect of surface oxide. Figure 4 shows the electrochemical oxidation of dissolved CO on a gold rotating disk at 1600-rpm when the returning potentials are changed at 0.8 V, 1.1 V and 1.4 V. The results clearly show that when the electrode

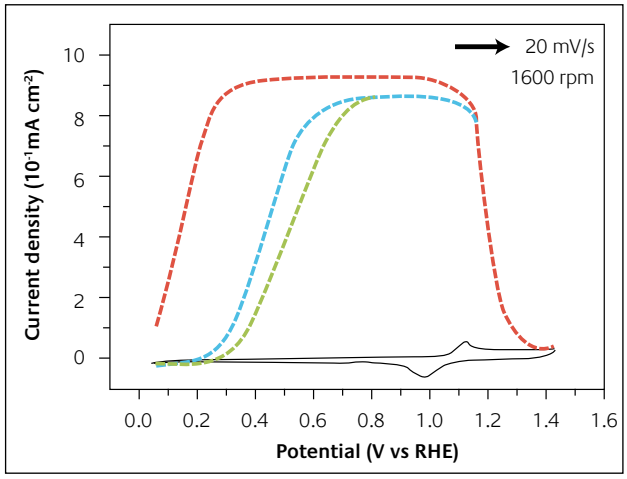

Figure 4

Rotating Disk data of gold disk at 1600 rpm in 10^{-3} M CO saturated KOH. Red line: potential window of 0.05-1.4V, blue line: potential window of 0.05-1.1V, and green line: potential window of 0.05-0.8V. (Positive potential scan recorded; solid line/no rotation).

potential has reached at 1.4 V, a potential beyond the surface oxide formation region, the oxidation for dissolved CO is enhanced. The enhancement probably results from the oxidation of impurities on the electrode surface or the synergetic effect of oxygen-containing species on the electrode surface. This enhancement was not seen when the oxidation potentials were reached only at 0.8 V or 1.1 V. In such cases, the effect of surface adsorbed CO becomes significance in retardation of the electrochemical oxidation of the dissolved CO due to the re-adsorption of CO in the scan period of potentials less than 1.1V and much less CO adsorption at oxide formation potential of gold above 1.1V.

In conclusion, our results demonstrate that electrochemical oxidation of dissolved CO on gold electrode is mainly diffusion-controlled process at the potential greater than 0.3V (vs. RHE). At the potential range between 0.0V and 0.3V, the oxidation process is a mixed-control process. Our data also confirm that the electrochemical oxidation of dissolved CO is affected by the presence of surface oxide on gold.

About the Authors

Andrew S. Lin is Associate Professor of Chang Gung University at Taiwan and he previously worked as a project leader of fuel cell program at Industrial Technology Research Institute after his residence at US Naval Research Laboratory.

Dr. Jerry Huang taught part-time in universities after his retirement from General Motors Research Center and he had more than 30 years experience in electrocatalysis and polymer electrolyte fuel cell. Both of them graduated from Case Western Reserve University

and worked with Prof. Ernest B. Yeager in 1970 and 1990. They were studying on platinum and platinum alloys as electrocatalysts in acidic electrolytes for many years before studying gold as electrocatalysts in alkaline system. Mr. Johnny Lin graduated from CGU years ago and now is working at Antig Fuel Cell Company (www.antig.com).

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